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(54) Title: RETENTION SYSTEM

(57) Abstract

There is provided a method for flocculating one or more particulate materials present in a dispersion, the method comprising contacting the dispersion with fibrous cationic colloidal alumina microparticles.

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Retention System

The present invention relates to a retention system. In particular the present invention relates to a method for flocculating one or more particulate materials present in a

5   dispersion.   The present invention utilises fibrous cationic colloidal alumina microparticles.

Retention aids are employed to bond the papermaking stock components together and reduce the loss to white water by either coagulation or flocculation of small particles,

10   and then entrapment or attachment of the flocs onto the larger cellulosic fibres. The papermaking stock is essentially a suspension of particles ranging from 2-3 mm down to a few nanometres in dimensions, the distribution of which depends on the type of filler used and the degree of refining and cleanliness of the pulp.

15   Charge neutralisation is the predominant mechanism in coagulation of small particles in papermaking stock. Retention has been recognised for many years as one of the most important aspects of papermaking. Careful application of retention aids may provide many process benefits and economic benefits, such as optimised wet-end running conditions, improved paper properties, maximised raw material yield, and reduced

20   effluent load.

In recent years trends in paper and board production have contributed to the need for improved retention systems. These trends have included the need for better paper quality, higher machine speeds, greater filler levels, the use of mechanical pulps and

25   recycled fibres and of course environmental pressures. This drive to improve sheet quality, increase paper machine productivity, and control rising furnish costs continues to escalate the demands placed on wet end chemistries.

Papermaking often compromises one desirable benefit in order to gain more of another

30   desired benefit. An example of this is use of single high molecular weight polymer drainage/retention aids on paper machines. Simple (single polymer) retention aid systems often lack flocculation power under highly turbulent conditions. To obtain high

retention of fines on high-speed paper machines, dual-polymer or microparticle retention systems have been developed. Dual-polymer retention aid systems have gained popularity particularly for the manufacture of low basis weight papers (e.g., tissue paper) or filler-containing papers (fine paper, magazine paper) under severe

5   retention conditions.

Dual-polymer systems have been used for many years with varying degrees of success. Generally speaking, they have comprised of a combination of the low molecular weight cationic polymer, such as a polyamide, and a high molecular weight anionic

10   polyacrylamide. The cationic polymer is normally added early in the stock to neutralise much of the anionic material present and create an environment in which the negatively charged (anionic) polyacrylamide can function effectively. The polyacrylamide functions by bridging flocculation and there may be a need to compromise between optimum retention and paper properties. Occasionally it is impossible to neutralise the

15   anionic material totally and cationic/cationic polymeric retention systems have been successfully employed.

Microparticulate retention aid systems are normally based on negatively charged inorganic colloids and positively charged synthetic or natural polymers. The main

20   difference between the systems is usually the type of microparticle used. Currently used commercial anionic microparticulate retention aid systems include

- Compozil - colloidal silica used in conjunction with cationic starch (available from EKA Nobel AB, Sweden); and

- Hydrocol - sodium montmorillonite (bentonite clay) used with cationic

25   polyacrylamide (available from Allied Colloids, UK).

The performance of chemical flocculants as retention aids in papermaking may depend on factors such as the point of addition and the shear levels experienced. A high shear level often leads to the break-up of flocs formed, which is beneficial for paper

30   formation, but it also leads to the detachment of fillers deposited on fibres and thus reduces filler retention. A high degree of reflocculation, especially with regard to the flocculation of fillers to fibres when the shear subsides is therefore a desirable

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characteristic of a retention aid system. This ability to reflocculate after floc breakage is a feature normally ascribed to the microparticle-containing flocculant systems.

In commercial microparticle systems, strong flocculation of fillers and fibres is first
5   achieved by addition of the cationic component, which is normally a high molecular weight polymer (e.g., cationic starch or cationic polyacrylamide). After periods of high shear, e.g., in pumps, screens, and pipe constrictions, during which flocs are partly disrupted to floc fragments, the flocs can reform when the high shear subsides. Close to the headbox, the negatively charged particle sol is added, which leads to greater
10   flocculation through charge interaction with the cationic polymers adsorbed onto particle surfaces.

The results of microparticulate coagulation can be very significant and even dramatic when compared to standard retention aid systems. They may include improved
15   retention (stronger flocculation), faster dewatering (drainage) on the wire and press section of the paper machine, greater overall control and flexibility and improved paper properties.

The retention of filler particles is of great economic and process benefit. However, it
20   also poses a complicated problem and it is difficult to predict the effect of changes in the wet-end of the papermaking system on the retention of filler. Selection of the best retention aid programme depends on the type of fillers used, filler loading, anionic trash content, type and amount of starch, whether the sheet is sized or not, and the mechanical shear of the machine, etc. Consideration also has to be given to the level of retention
25   desired, and the corresponding loss in formation allowable. Increased retention leads to higher chemical costs, so the payback in terms of increased productivity and filler saving is a factor. Reliable selection of a suitable retention aid system is largely dependent on the chemistry of the system.

30   To-date much of the literature on microparticle applications in the papermaking industry has concerned anionic microparticles used in conjunction with a high molecular weight cationic polymer. However, a synthetic cationic polymeric microparticle with a range of

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particle sizes and charge densities has been used as a retention aid for negatively charged fibres and positively charged precipitated calcium carbonate particles [H Ono and Y Deng, 1996 CPPA International Paper and Coating Chemistry Symposium, Canada, pp 175-184, 11-13 June (1996)].

5

Colloidal silica has previously been treated to make it cationic, and used as a retention aid system in conjunction with either an anionic or cationic polymer [K Moberg, TAPPI Papermakers Conference Proceedings, Volume 1, 115-127, (April 1993), TAPPI Press, Atlanta, GA]. This system has not been commercialised.

10

Cationic colloidal silica microparticles, where aluminium atoms have replaced some of the surface silica, are also known. US-A-4798653 describes a system where anionic polyacrylamide is used with a cationic silica sol, where the polyacrylamide dosage ranges from 0.01 to 1.0% w/w, and the microparticle between 0.01 and 2.0% w/w. It is

15 recommended that the polymer has a medium to high molecular weight and low charge density.

A similar cationic colloidal silica is described in US-A-4946557. This teaching uses a cationic polyacrylamide. The order of addition of the two components is largely

20 influenced by the size of the silica particles. Better results are reported with small silica particles when the polymer is added first, but for larger particles the silica should be added first.

Silica-containing anionic microparticulate systems can be expensive in use. Moreover,

25 silica sols rendered cationic by incorporation of polyvalent metallic ions (e.g., Al^{3+}) in the silica surface are unstable with respect to disproportionation under normal conditions of use and either have to be prepared and used quickly or require the use of additional stabilising components such as phosphate, carbonate, borate and the like. [US-A-4798653: US-A-4946557]

A major disadvantage of bentonite-containing anionic microparticulate systems is that bentonite (Na^+-montmorillonite) is classed as a carcinogen, so particular care must be taken in its handling and transportation [K Johnson. In: 51st APPITA Annual General Conference Proceedings, pp 325-328, 28 April - 2 May 1997].

5   The present invention addresses the problem of the prior art.

Aspects of the present invention are defined in the appended claims.

10   In the present specification by the term "alumina" it is meant any compound comprising aluminium and oxygen. Preferably the compound consists essentially of aluminium and oxygen.

The alumina may be α-alumina, β-alumina, γ-alumina or a mixture thereof. Preferably
15   the alumina is acicular (fibrous) boehmite alumina (α-alumina). In this aspect preferably the acicular (fibrous) boehmite alumina (α-alumina) may be obtained under acidic hydrothermal conditions (according to US 2915475 or WO 97/41063).

Preferably the alumina is fibrillar hydrated α-alumina, known as boehmite alumina
20   (formula: α-AlOOH) or basic alumina monohdrate, optionally obtained in accordance with a process described in WO 97/41063. The fibrils each consist of a crystal of boehmite alumina. The particles contain surface-bound acetate groups (chemisorbed CH_2COO^-) and have a high positive surface charge which is responsible for the colloidal stability of the system and the other useful properties of the product. In water, these
25   cationic boehmite colloid particles are stabilised by electrical double-layer repulsion.

In the present specification by the term "fibrous" it is meant products which are composed of fibres.

30   The term "fibre" is used in accordance with the customary meaning and includes fibrils and aggregates of fibrils which form relatively long thread-like structures.

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The term "fibril" is used to refer to products which when viewed under the electron microscope appear to be single particles as opposed to structures formed of aggregates of a number of separate members. The term "fibrous" encompasses materials in which the fibrils are discrete and relatively unaggregated.

Preferably the fibrils are particles with an aspect ratio of ≥ 3:1, preferably ≥ 20:1 and/or preferably with a uniformity of diameter along the length of the particle. Depending on the specific process conditions used in preparation, the fibrous alumina may be in the form of fibrils or small fibres which have one or more dimensions in the colloidal range. Such fibrils can form aggregates of larger fibres made up of assemblies of fibrils disposed parallel to the length of the fibres. Such fibrous alumina as used in the present specification will preferably have the boehmite crystal lattice.

In the present specification by the term "microparticles" it is meant particles having an average maximum dimension of 1000nm.

Preferably the "microparticles" are non-deformable particles (spherical, plate-like or fibrous in shape)

In the present specification by the term "cationic" it is meant that the compound/composition is ionic and has a positive charge.

In the present specification by the term "colloidal" it is meant a heterogeneous system consisting of one substance (the disperse phase) finely divided and distributed throughout a second substance (the continuous phase). Generally speaking, the disperse phase has dimensions in the range of 1 to 1000 nm (1μm).

The present invention may provide a fibrous cationic colloidal alumina useful in retention, drainage and dewatering of papermaking that is stable in storage, safe to use and cost-effective.

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The present invention may provide a composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) an anionic substance and a method for using the same or the constituents thereof to improve the effectiveness in retaining the fine mineral fillers such as calcined clay with paper fibres using a new retention system based on a synthetic water-based fibrous colloidal alumina with a high surface charge.

The present invention may provide a drainage/retention aid composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) an anionic substance and a method for using the same or the constituents thereof that is less shear- and pH-sensitive as compared to conventional drainage/retention aides comprising high molecular weight cationic acrylamide-derived polymers.

The present invention may provide a new inorganic cationic microparticulate retention composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) an anionic substance and a method for using the same or the constituents thereof to improve the effectiveness in retaining fine mineral fillers such as calcined clay with paper fibres,

The present invention may provide a synthetic water-based colloidal alumina composition with high positive surface charge and controllable particle size and a method for using the same or the constituents thereof. The composition may be useful in wet-end papermaking processes, particularly for the retention of fine particulate fillers such as calcined clay.

The flocculant system of the present invention (i.e. a composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) an anionic substance) and the method for using the same was found to be relatively resilient to shear stress and insensitive to common papermaking process pH variations. This new flocculant system and method was found to give comparable results to a commercial anionic microparticle system in terms of retention and sheet formation when compared on a pilot paper machine and in the laboratory.

The flocculant system and method of the present invention is stable under normal conditions of storage and use and does not present handling problems nor require application of additional stabilising components.

5   Unlike most other microparticles used in the papermaking industry, the flocculant system of the present invention is cationic and fibrous in shape. Consequently, there is little or no conformational changes of the alumina fibres once adsorbed or for reduced effects from penetration into the pores of cellulosic fibres, due to the rigid structure of the alumina particles.

10

Without being bound by theory it is believed that the high positive surface charge on the colloid provides rapid interaction and exhaustion onto negatively charged surfaces, such as cellulosic fibres in this application. Such surfaces 'coated' with the colloidal alumina will, in turn, anchor other negatively charged materials, such as anionic polymers as

15   used in this invention.

Furthermore, the other advantages of using the positively charged flocculant system of the present invention instead of water-soluble retention aids include more effective patch formation on adsorption and higher charge density which may be easily

20   controllable by the synthesis chemistry.

The total cationic demand of the pulp furnish in papermaking can be reduced by using cationic microparticles and there is no accumulation of the microparticles in a closed white water system because of the strong adsorption of the cationic sol onto negatively

25   charged substrates.

As discussed above the flocculant system of the present invention comprises an anionic (negatively charged) material which may effect retention flocculation of the one or more particulate materials, such as fillers. As for the broadest aspect of the present invention,

30   this may be performed in the presence or absence of cellulosic fibres.

Without being bound by theory it is believed that the positively charged sol acts to change the surface charge of cellulosic fibres and the like (including filler particles) from negative to positive. The anionic substance, such as the negatively charged polymer, then acts to flocculate the mixture by electrostatic interaction.

5

Suitable anionic substances can include both polymers and colloidal inorganic materials. Suitable anionic inorganic materials include but are not limited to particulate silicaeous materials, clays, calcium carbonate, anionic alumina, titania, zirconia and the like known in the art, and mixtures thereof. Anionic polymeric co-additives are preferred

10 and include starches, anionic polyacrylamides, polyacrylates, carboxymethylcellulose, and the like known to those skilled in the art, and mixtures thereof.

The preferred anionic polymers comprise polyacrylamide, or mixture of polyacrylamides, having a molecular weight in excess of 100,000 and preferably

15 between about 5,000,000 and 15,000,000. The anionicity (degree of carboxyl fraction present) of the polyacrylamide may range between about 1 to about 40%. An example of particularly suitable organic anionic polymeric materials for use in the present invention are those commercially available from Allied Colloids under the tradename 'Percol'.

20

The anionic polymer may form a co-bridge with the alumina, which will significantly increase flocculation efficiency.

As described above the flocculant system and method of the present invention was

25 found to be relatively resilient to shear stress and insensitive to pH variations. The flocculant system of the present invention comprising both alumina and anionic polymer was found to be particularly resilient to shear stress and insensitive to common papermaking process pH variations. This dual system was found to give comparable results to a commercial anionic microparticle system in terms of retention and sheet

30 formation when compared on a pilot paper machine and in the laboratory.

Neither the particle size nor surface charge of the cationic microparticles is, alone,

critical to the performance of the present invention.   The present invention is advantageous provided the microparticles can disperse and be dispersed in the suspension, such as an aqueous pulp suspension, and can readily interact with the components which are present in the suspension or the anionic substances of the
5   invention.

The microparticles of the present invention may form or be in the form of water-insoluble dispersions. In such dispersions the microparticles any exist both as discrete particles and aggregates of said particles.

10

In a preferred aspect the microparticles have surface area of greater than $500m^2/g$.

Without being bound by theory it is believed that the cationic particle sols in the microparticle retention system induce flocculation through electrostatic interaction with
15   the anionic substance, such as a high molecular weight polymer.

The microparticles may be in one aspect of the present invention inorganic colloidal particles.

20   The dosage amount of cationic microparticles and/or the anionic material, such as anionic polymers. used in this invention, is not, per se. critical to the performance of the present invention. Generally the dosage is controlled to be in an amount to flocculate the suspended matter. Those of ordinary skill in the art can readily determine suitable dosage amounts by conventional means. Thus, whilst the exact dosage amount for a
25   particular system can vary widely depending on the nature of the system, the amount of suspended matter and the degree of drainage or retention desired. In general the dosage, based on the dry weight of suspended matter amount, can range:

• for the alumina, from 0.05 to 3% w/w, preferably from 0.1 to 2% w/w

• for the anionic material, from 0.005 to 0.5 weight percent. preferably from 0.01 to
30   0.3% w/w.

Preferably the anionic material:alumina ratio may be from 1:1 to 1:10. more preferably from 1:2 to 1:5, yet more preferably approximately 1:4.

It seems that the order of addition of the alumina and the anionic material may have some influence on the obtained effect. In a preferred embodiment of this invention the alumina is generally added first and the anionic material added subsequently.

The method of the present invention can be carried out over a wide pH range. In a preferred aspect, the suspension has a pH of from 4 to 9.

The present invention is suitable for use with pulps of both hardwoods or softwoods or combinations thereof. Pulps of the chemical, mechanical. semichemical or thermomechanical types are suitable for treatment in accordance with the present process.

We have found the present invention to be advantageous in providing useful wet-end papermaking properties, particularly for the retention of fine particulates.

The invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

Figure 1 shows a graph.
Figure 2 shows a graph.
Figure 3 shows a graph.
Figure 4 shows a graph.
Figure 5 shows a graph.
Figure 6 shows a graph.
Figure 7 shows a schematic.

The following preparations and examples are included herein as further description and are illustrative of the present invention.

<u>**EXAMPLES**</u>

PREPARATION OF COLLOIDAL ALUMINA SAMPLES

Example 1 - Electrophoretic Mobility and Particle Size Measurements

5

A series of seven cationic colloidal alumina samples (tradename Octasol™ marketed by The Associated Octel Company Limited) of varying surface charge and particle sizes were prepared according to the methods exemplified in WO 97/41063. In particular, preferably these cationic colloidal alumina samples were made from isolated solid basic

10   aluminium acetate or other similar aluminium containing salt or starting material under acidic hydrothermal conditions. The electrophoretic mobility and the zeta potential of the sample particles were determined using a Coulter Doppler Electrophoretic Light Scattering Analyser model 440 (DELSA) which uses a combination of electrophoresis (movement in an applied electric field) and laser Doppler velocimetry (Table 1). The

15   particle sizes of the samples were measured using a Coulter LS130 Laser Sizer. The samples in Table 1 were diluted to 0.2%w/w alumina in 6% w/w acetic acid solution for the electrophoretic mobility measurements.

Table 1 Alumina Colloid Zeta Potentials And Particle Sizes

Sample	DELSA Mobility* (μm.cm/Vs)	Zeta Potential* (mV)	Particle Size† (number mean, μm)
PP-1	6.24	79.9	1.524
PP-2	6.16	79.0	0.918
PP-3	6.16	79.0	1.490
PP-4	7.75	99.5	1.491
PP-5	6.74	86.5	0.171
PP-6	6.31	81.0	0.174
S2-9A	6.64	85.2	0.167

20

* measured at cell centre

† measured in 1% acetic acid solution

FLOCCULATION STUDIES

A Photometric Dispersion Analyser (PDA 2000, Rank Brothers, UK) was used for analysing suspension flocculation in conjunction with a standard propeller-type Dynamic Drainage Jar (DDJ) fitted with a 70-mesh screen. The basis of the PDA is the measurement of the turbidity of a flowing suspension, by measuring the amount of light transmitted through it and converting the transmitted light to an output voltage signal proportional to the intensity (Beer Lambert Law). There are two components to the output voltage, a large dc component and a much smaller fluctuating ac signal. The dc signal is a measure of the turbidity of the suspension since it corresponds to the average transmitted light intensity. From the fluctuating ac signal, the rms value is derived which has been shown to indicate the state of aggregation. The rms value is related to the average number concentration, the nature and size of suspended particles. In order to compare the flocculation induced, the relative turbidity, t_f, of the final suspension to the unflocculated filler suspension, t_i, was used. The lower the value obtained from the relative turbidity, t_f, the better the flocculation. The relative floc size V_{rms}/V derived from the root mean square of the fluctuation ac signal of the PDA has also been used to estimate the efficiency of flocculation (aggregation) in the clay filler experiments.

The PDA/DDJ system was used to examine the effectiveness of the different alumina samples in flocculating clay filler particles in the absence and presence of papermaking fibres and in the presence and absence of common commercial retention polymers.

A 5%w/w filler slurry with distilled water was made up. All colloidal alumina samples and polymers were freshly made up to 0.2%w/w with distilled water. Alphatex clay was supplied by English China Clays International. Where used, a 0.5%w/w pulp suspension was prepared using 50% Lapponia Pine and 50% Birch pulp. The pulp was disintegrated using the Standard Disintegrator to separate the fibres but not to refine. Where retention polymers were used, the solid grade products supplied were prepared to 0.2%w/w solutions using the methods recommended by the supplier.

Example 2 - Clay Filler Flocculation Studies with Microparticulate Alumina Alone

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The optimum dosage of colloidal alumina to clay filler for these studies was found to be 0.7%w/w on clay in flocculation experiments using 5%w/w clay suspension in the absence of fibres and colloidal alumina at levels of 0.1 to 3.0%w/w (Table 2). The relative turbidity decreases rapidly as the alumina dosage increases and levels out at around 0.7-1.0%w/w on clay (Figure 1). Above 1.0%w/w on clay there is little further change in the relative turbidity.

The relative floc size given by V_{rms}/V values show a steady increase as the colloidal alumina dosage increases (Figure 2).

Table 2 Alphatex Clay Flocculation with Octasol™ (No Fibres present)

Relative Turbidity (Tf/Ti)						
Dose:	0.00%	0.1%	0.4%	0.7%	1%	2%	3%
PP1	1.00	1.00	0.88	0.81	0.78	0.79	0.78
PP2	1.00	0.99	0.93	0.85	0.83	0.74	0.63
PP3	1.00	1.00	0.91	0.81	0.82	0.79	0.75
PP4	1.00	1.00	1.00	0.94	0.89	0.88	0.92
PP5	1.00	1.01	0.99	0.88	0.86	0.86	0.86
PP6	1.00	1.00	0.91	0.83	0.81	0.80	0.81

Vrms/V						
Dose:	0.00%	0.1%	0.4%	0.7%	1%	2%	3%
PP1	0.04	0.03	0.07	0.10	0.15	0.20	0.25
PP2	0.04	0.04	0.06	0.10	0.13	0.19	0.24
PP3	0.04	0.04	0.06	0.09	0.12	0.20	0.22
PP4	0.04	0.04	0.04	0.03	0.03	0.05	0.06
PP5	0.04	0.04	0.03	0.03	0.04	0.06	0.07
PP6	0.04	0.04	0.04	0.07	0.08	0.13	0.16

Example 3 - Clay Filler Flocculation Studies with Microparticulate Alumina in Combination with Retention Polymers

5   The flocculation of 5%w/w clay suspension in the absence of fibres was studied (Table 3), using the colloidal alumina at 0.7%w/w on clay in combination with the commonly used anionic retention aid polymer Percol E24 (a medium molecular weight anionic polyacrylamide with medium charge density available from Allied Colloids) at varying polymer dosages (0-0.7%w/w on clay). The effect of the use of the polymer alone at

10   each dosage was also examined.

Figure 3 shows great synergy with all dual component systems of Percol E24 and various microparticle samples studied giving greatly reduced turbidity below each single component system, at all polymer dosages used. The results given in Figure 3 show that

15   the use of the anionic polymer alone on clay gives poor flocculation in this system. The system at a low polymer dosage appears to be as effective than at a higher dose. The optimum dosage of flocculants was found to be 0.875%w/w on clay (at Octasol™:PercolE24 ratio 4:1).

20   Figure 4 shows the relative clay floc size from the V_{rms}/V value in the anionic polymer:cationic colloidal alumina system. As with the relative turbidity curves (Figure 3), there appears to be little dependence of the polymer dosage on the clay floc size. However, whilst the turbidity drops significantly when the anionic polymer is added to the clay after the colloidal alumina, the floc size does not appear to grow significantly.

25   This may be of advantage in consideration of final sheet formation.

Table 3 Clay Flocculation with Octasol™ and Anionic Retention Polymer

Relative Turbidity (Tf/Ti)					
Polymer Dose	0	0.18	0.35	0.53	0.70
Polymer Alone	1.00	0.91	0.93	0.94	0.91
PP1 + Polymer	0.82	0.10	0.16	0.19	0.14
PP3 + Polymer	0.81	0.08	0.08	0.07	0.09
PP4 + Polymer	0.94	0.21	0.20	0.27	0.26
PP6 + Polymer	0.84	0.06	0.11	0.09	0.09
S2-9A + Polymer	0.74	0.05	0.08	0.10	0.12
Vrms/V					
Polymer Dose	0	0.18	0.35	0.53	0.70
Polymer Alone	0.04	0.03	0.04	0.04	0.04
PP1 + Polymer	0.10	0.08	0.11	0.06	0.04
PP3 + Polymer	0.09	0.04	0.05	0.03	0.04
PP4 + Polymer	0.03	0.08	0.08	0.12	0.09
PP6 + Polymer	0.07	0.03	0.09	0.06	0.05
S2-9A + Polymer	0.07	0.04	0.08	0.12	0.12

Example 4 - Effect of Order of Addition

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With the anionic polymer Percol E24, better results were obtained when the microparticulate alumina is added to the clay suspension first, at the ratio of 1:4 as can be seen from the values of the final relative turbidity given in Table 4.

Table 4 Comparison of Addition Order with Octasol™ and Anionic Polymer

Order	Final Relative Turbidity			
of Addition	PP-1	PP-3	PP-4	PP-6
Octasol™ added first	0.10	0.08	0.21	0.06
Octasol™ added second	0.34	0.35	0.47	0.35

Example 5 - Clay Flocculation in the Presence of Fibres

Anionic Percol E24 polymer was used as a dual retention system with Octasol™ in this laboratory study. The microparticle dosage was fixed at 0.7%w/w on clay and polymer at 0.175%w/w on clay giving a polymer:microparticle ratio of 1:4. In each case the alumina was added to the premixed clay and fibre suspension as the first component, prior to the addition of the anionic polymer. The relative turbidities for a dual system of Octasol™ and anionic Percol E24 are given in Table 5.

Table 5 Dual Component Induced Clay Flocculation with Fibres

Component	Relative Turbidity
Percol E24	0.60
Percol E24:PP-1 (ratio 1:4)	0.35
Percol E24:PP-3 (ratio 1:4)	0.31
Percol E24:PP-4 (ratio 1:4)	0.39
Percol E24:PP-6 (ratio 1:4)	0.33
Percol E24:S2-9A (ratio 1:4)	0.11

Table 5 shows that all the anionic polymer dual component systems gave a reduced turbidity over the use of anionic polymer alone at the dosage of 0.7%w/w alumina on clay at the polymer:microparticle ratio of 1:4.

Example 6 - Effect of Other Anionic Polymers

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The effect of varying the properties (molecular weights and charge densities) of the anionic polymer used in a dual retention system is shown in Table 6. In each case the effect of using the dual component retention system is to reduce the relative turbidity of the system over use of polymer alone.

Table 6 Effect of Varying Anionic Polymer on Effectiveness of Dual Component Retention System

Polymer	Polymer Charge Density	Molecular Weight	Relative Turbidity		
			Polymer Alone	PP-3/ Polymer	S2-9A/ Polymer
Percol 173	DS 5%	12,000,000	0.30	0.12	0.01
Percol 338	DS 10%	18,000,000	0.19	0.07	-
Percol E24	DS 15%	14,000,000	0.60	0.31	0.11
Percol 156	DS 30%	16,000,000	0.51	0.27	0.05

Octasol™, 0.7%w/w on clay (0.14%w/w on fibre); polymer 0.175%w/w on clay; 5%w/w clay suspension; 0.5%w/w pulp slurry; 20% clay on fibre.

Example 7: Effect of pH on Clay Flocculation with Fibres

The results of varying the pH on the single component colloidal alumina system, PP-3, the single component anionic polymer Percol 173, and the dual component polymer/Octasol™ system are shown in Figure 5. Figure 5 shows that the relative turbidity of the clay and fibre suspension filtrate in the dual component system is greatly reduced below that of either of the single components.

Over the pH range commonly employed in papermaking of pH 6-9, spanning both acidic and alkaline processes, there is little pH dependence when Octasol™ is used alone. The anionic polymer, Percol 173, alone appears to be much more dependent on pH, with its performance significantly impaired as the pH rises. The dual component system

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possesses some pH dependency, probably as a result of the sensitivity of the polymer to pH, but even at the very high pH of 10, the relative turbidity of the clay and fibre suspension filtrate is greatly reduced below that of either of the single components. Over the range of pH 6-9 the relative turbidity of the dual component system is quite favourable and thus it can be deduced that similar results in terms of flocculation may be achieved in both acidic and alkaline papermaking processes.

Example 8: Effect Of Shear On Flocculation

The effect of shear on the filler flocculation in the presence of fibres was examined by varying the DDJ propeller stirring speed from 500 rpm to 1500 rpm which should cover the shear rates experienced on most commercial papermachines, as shown in Figure 6.

It can be seen that for PP-3 alone, the shear rate has little effect on the relative turbidity of the suspension. This suggests that the clay flocs formed by Octasol™ alone are resilient to the effects of shear, perhaps due to their small size and strong binding between the cationic microparticles and the clay. By contrast, the Percol 173 polymer alone appears to form flocs which degrade in size as shear increases. This is likely to be as a result of larger flocs formed by bridging flocculation. With the dual component systems the relative turbidity increases as the shear rate rises, until above about 1000 rpm where it tends to level off. This has practical implications in that if the flocs are resilient to shear, then retention will not drop off due to turbulence in the head-box or vibration of the wire.

To further investigate the effects of addition order and shear on the resultant clay floc size, tests with cationic Octasol™ PP-3 and anionic Percol 173 under various shear conditions were conducted. The first component was added to the clay suspension with the DDJ stirring rate at 500rpm, and a flocculated clay Sample 1 withdrawn from the DDJ for size analysis using the LS130. The stirring rate was then increased to 1500rpm for 60 seconds before Sample 2 was withdrawn, and finally the second retention component was added with the stirring rate returned to 500rpm, and Sample 3 was taken. The results are shown in Table 7.

Table 7: Octasol™ PP-3 and Anionic Percol 173 Clay Floc Sizes

Anionic Percol 173 and Octasol™ PP-3		Octasol™ Added First	Percol 173 Added First
Sample 1 - 500 rpm	LS130 Volume Mean Size (mm)	3.821	5.078
Sample 2 - 1500 rpm	LS130 Volume Mean Size (mm)	3.855	4.672
Sample 3 - 500 rpm	LS130 Volume Mean Size (mm)	15.38	20.96

5   The addition of Octasol™ added after the anionic polymer results in very large clay flocs which may be detrimental to the finished sheet formation, but when Octasol™ is added as the first component, the results are more favourable.

The use of Octasol™ as the first component appears to give small, shear-resistant flocs, 10 as their size remains fairly similar after high shear is applied. The cationic Octasol™ microparticles bridge between the clay particles via their negatively charged surfaces. The bridge length is short, due to the small microparticle size, resulting in flocs that are small and not broken down easily. The rigid nature of the microparticles makes it such that they cannot flatten against the surface of the clay particles, but retain a discrete 15 positive charge for interaction with the anionic polymer. Thus when anionic Percol 173 is added the floc size grows, probably as a result of the polymer bridging between the small flocs either by the cationic Octasol component of the floc, or the cationic edges of the clay platelets.

PAPERMAKING STUDIES

A papermachine trial was carried out using Octasol™ samples PP-3 and S2-9A in conjunction with anionic Percol 173.

The machine trial used a 50% mixture of hardwood and softwood, Lapponia pine and birch. The thickstock was refined continuously using the in-line disc refiner. Alphatex clay was dosed into the thickstock after the disc refiner as a 25 %w/w slurry, but prior to the high shear conical refiner. The purpose of the conical refiner was simply to act as a mixer, providing no additional refining to the stock. The first retention aid component (Octasol™) was added to the clay and thickstock prior to the conical refiner, and the second component (Percol) was dosed into the headbox, as shown in Figure 7.

The backwater, headbox and thickstock samples were analysed for total solids and ash content in order to determine First Pass Retention (FPR) and First Pass Ash Retention (FPAR).

Example 9 Pilot Papermachine Trial Results

Table 8 gives the FPR and FPAR for Octasol™ and Percol 173 where the actual polymer:PP-3 ratio was kept fixed at 0.16, but the total dosage of the two components was reduced from 0.132 to 0.026 %w/w on o.d. fibre. The FPR and FPAR are seen to decrease with decrease in total concentration. The highest dosage of 0.132%w/w on o.d. fibre shows a dramatic increase in retention above the control situation of no retention aids (FPR = 82-84, FPAR = 9-17). A moderate total dosage of 0.072%w/w on o.d. fibre gives both good retention at no cost to the formation.

Table 8: Machine Trial Performance for Octasol™ and Percol 173 at Fixed Ratio

Run	Retention Aids	Total Dosage*	Ratio#	PDA t_r	FPR (%)	FPAR (%)	Formation Index
3	Percol 173:PP3	0.132	0.16	0.34	93.9	70.5	55.2
4	Percol 173:PP3	0.072	0.16	0.50	90.1	54.7	66.8
5	Percol 173:PP3	0.026	0.16	0.78	84.2	18.3	62.0

* Total component dosage (%w/w on o.d. fibre) for PDA: Run 3 - 0.13%; Run 4 - 0.07%; Run 5 - 0.025%

\# Actual polymer:Octasol™ ratio for PDA: Run 3 - 0.25; Run 4 - 0.25; Run 5 - 0.25

Table 9 compares the effect of changing the polymer:Octasol™ ratio at similar total dosages of 0.13%w/w on o.d. fibre. As the ratio increases, i.e. more anionic polymer is added for a given amount of Octasol™, the retention increases, although only slightly for the FPR, and a noticeable improvement in the sheet formation is observed at the highest polymer:Octasol™ ratio of 0.31. The use of the polymer on its own at a slightly lower dosage (Run 2) causes worse formation. This confirms that the synergy between Octasol™ and Percol 173 plays a significant role in improving the formation.

Table 9: Machine Trial Performance for Octasol™ PP-3 and S2-9A

Run	Retention Aids	Total Dosage*	Ratio#	PDA t_r	FPR (%)	FPAR (%)	Formation Index
3	Percol 173:PP3	0.132	0.16	0.34	93.9	70.5	55.2
4	Percol 173:PP3	0.072	0.16	0.50	90.1	54.7	66.8
5	Percol 173:PP3	0.026	0.16	0.78	84.2	18.3	62.0
7	Percol 173:PP3	0.126	0.31	-	94.8	74.4	63.4
8	Percol 173:PP3	0.137	0.08	-	92.7	63.5	55.4
11	Percol 173:S2-9A	0.148	0.14	0.01	94.3	72.8	57.6
12	Percol 173:S2-9A	0.080	0.14	-	90.4	56.5	60.7
13	Percol 173:S2-9A	0.155	0.07	-	94.6	73.0	55.7
2	Percol 173	0.025	-	0.41	87.7	40.0	60.1

5   *   Total component dosage (%w/w on o.d. fibre) for PDA: Run 3 - 0.13%; Run 4 - 0.07%; Run 5 - 0.025%; Run 11 - 0.14%

    #   Actual polymer:Octasol ratio for PDA: Run 3 - 0.25; Run 4 - 0.25; Run 5 - 0.25; Run 11 - 0.25

10

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in

5   connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

10

CLAIMS

1. A method for flocculating one or more particulate materials present in a dispersion, the method comprising contacting the dispersion with

(i) fibrous cationic colloidal alumina microparticles; and

(ii) an anionic substance.

2. A method according to claim 1 wherein the dispersion is aqueous based.

3. A method according to claim 1 or 2 wherein the dispersion comprises or is components of papermaking stock.

4. A method according to claim 3 wherein the papermaking stock is a pulp of a hardwood or of a softwood, or a combination thereof.

5. A method according to claim 4 wherein the pulp is selected from pulps of the chemical, mechanical, semichemical or thermomechanical types, or mixtures thereof.

6. A method according to any one of the preceding claims wherein the one or more particulate materials are flocculated on a fibrous material.

7. A method according to claim 6 wherein the fibrous material comprises or is fibrous cellulose.

8. A method according to any one of the preceding claims wherein the dispersion is contacted with a composition comprising

(i) fibrous cationic colloidal alumina microparticles; and

(ii) an anionic substance.

9. A method according to claim 8 wherein the anionic substance is an inorganic material

selected from particulate silicaeous materials, clays, calcium carbonate, anionic alumina, titania, zirconia, and mixtures thereof.

10 A method according to claim 8 wherein the anionic substance is a synthetic or a naturally derived polymer selected from starches, anionic polyacrylamides, polyacrylates, carboxymethylcellulose, and mixtures thereof.

11. A method according to claim 10 wherein the anionic polymer comprises a polyacrylamide, or a mixture of polyacrylamides, having a molecular weight in excess of 100,000 and preferably between about 5,000,000 and 15,000,000.

12. A method according to claim 11 wherein the anionicity (degree of carboxyl fraction present) of the polyacrylamide is from 1 to 40%.

13. A method according to claim 10, 11 or 12 wherein the polymer:microparticle ratio is from 1:1 to 1:10, preferably 1:2 to 1:5, more preferably approximately 1:4.

14. A method according to any one claims 8 to 13 wherein the dispersion is contacted with the cationic alumina prior to contact with the anionic substance.

15. A method according to any one of the preceding claims wherein the dispersion has a pH of from 4 to 9.

16. A method for retention and/or drainage of a papermaking stock as defined in any one of the preceding claims.

17. Use of fibrous cationic colloidal alumina microparticles for flocculating one or more particulate materials present in a dispersion.

18. Use according to claim 17, characterised by the features of any one of claims 2 to 16.

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19. A composition comprising

(i) fibrous cationic colloidal alumina microparticles; and

5   (ii) an anionic polymer.

20. A composition according to claim 19 wherein the anionic polymer is a polyacrylamide.

10   21. A retention system comprising fibrous cationic colloidal alumina microparticles.

22. A retention system according to claim 21 further comprising an anionic substance.

23. A retention system according to claim 23 wherein the anionic substance is

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(i) an inorganic material selected from particulate silicaeous materials, clays, calcium carbonate, anionic alumina, titania, zirconia, and mixtures thereof; or

(ii) a synthetic or a naturally derived polymer selected from starches, anionic

20   polyacrylamides, polyacrylates, carboxymethylcellulose, and mixtures thereof.

24. Paper or a paper product obtained or obtainable using the invention as defined in any one the preceding claims.
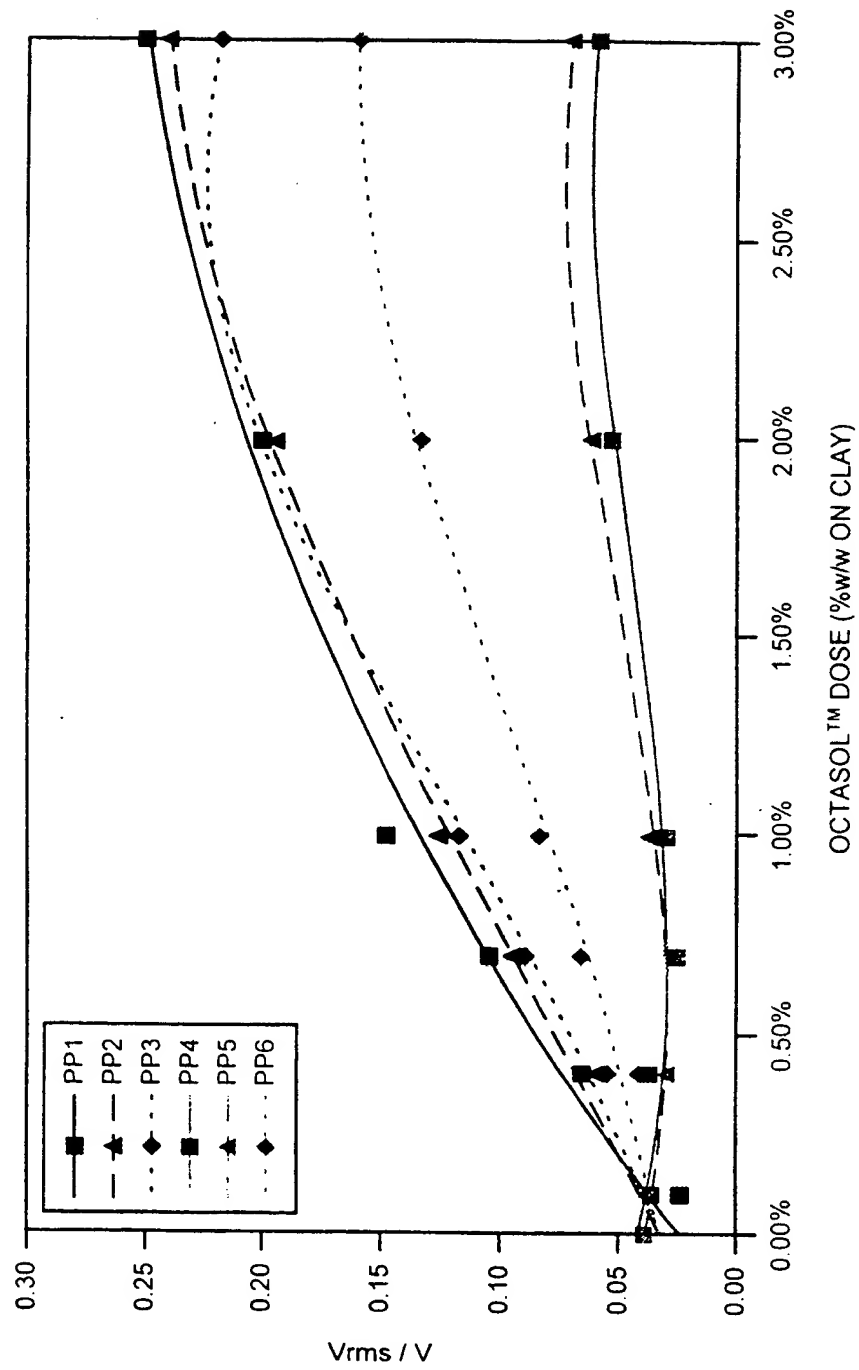
25   25. A flocculated particulate material obtainable by the method according to claim 1 or any claim dependent thereon.

FIG. 1

CLAY RELATIVE TURBIDITY AT VARYING OCTASOL™ DOSAGE
(NO FIBRES)
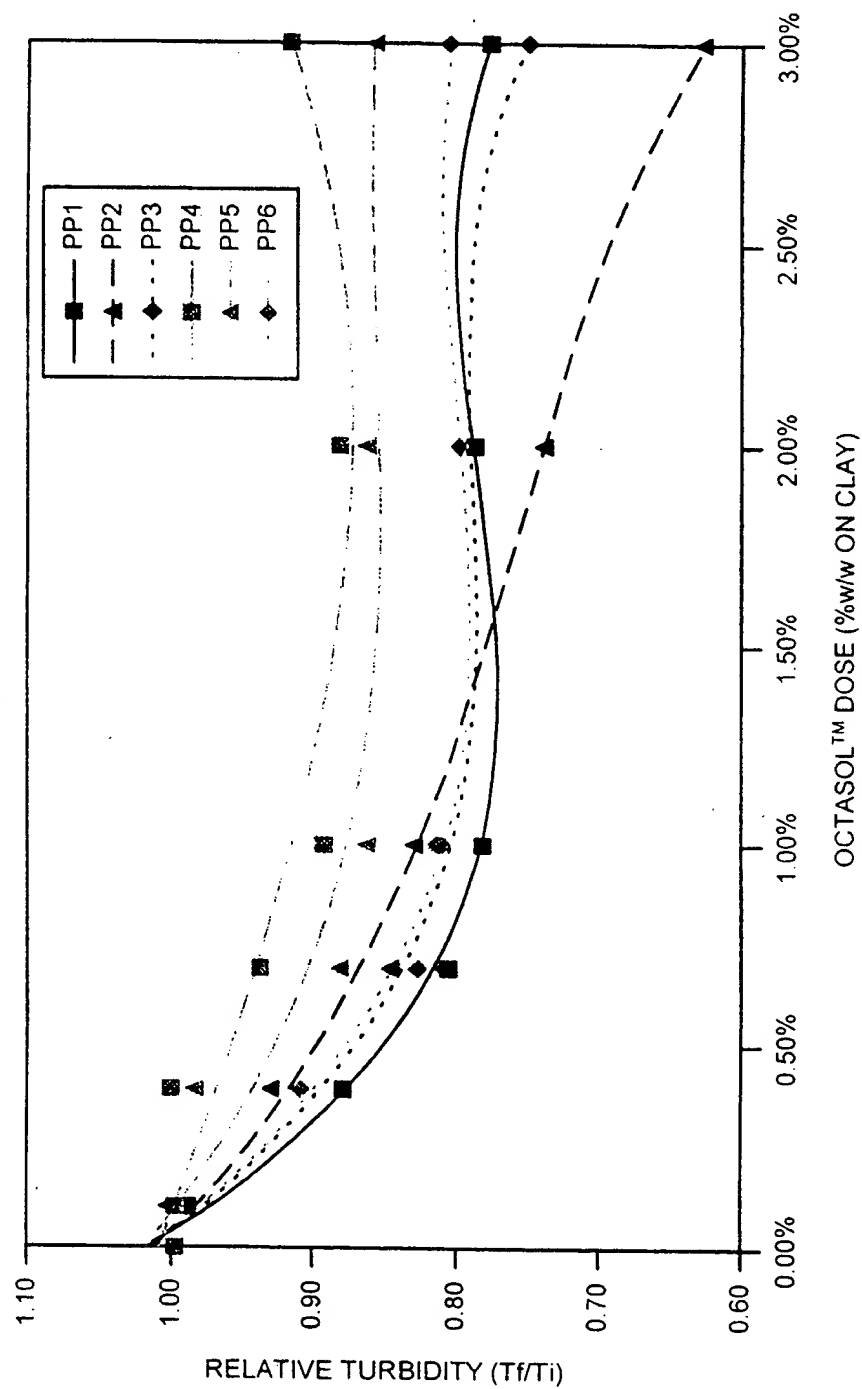
FIG. 2

CLAY FLOCCULATION AT VARYING OCTASOL™ DOSAGE
(NO FIBRES)

FIG. 3

CLAY RELATIVE TURBIDITY WITH OCTASOL™ AND ANIONIC PERCOL E24
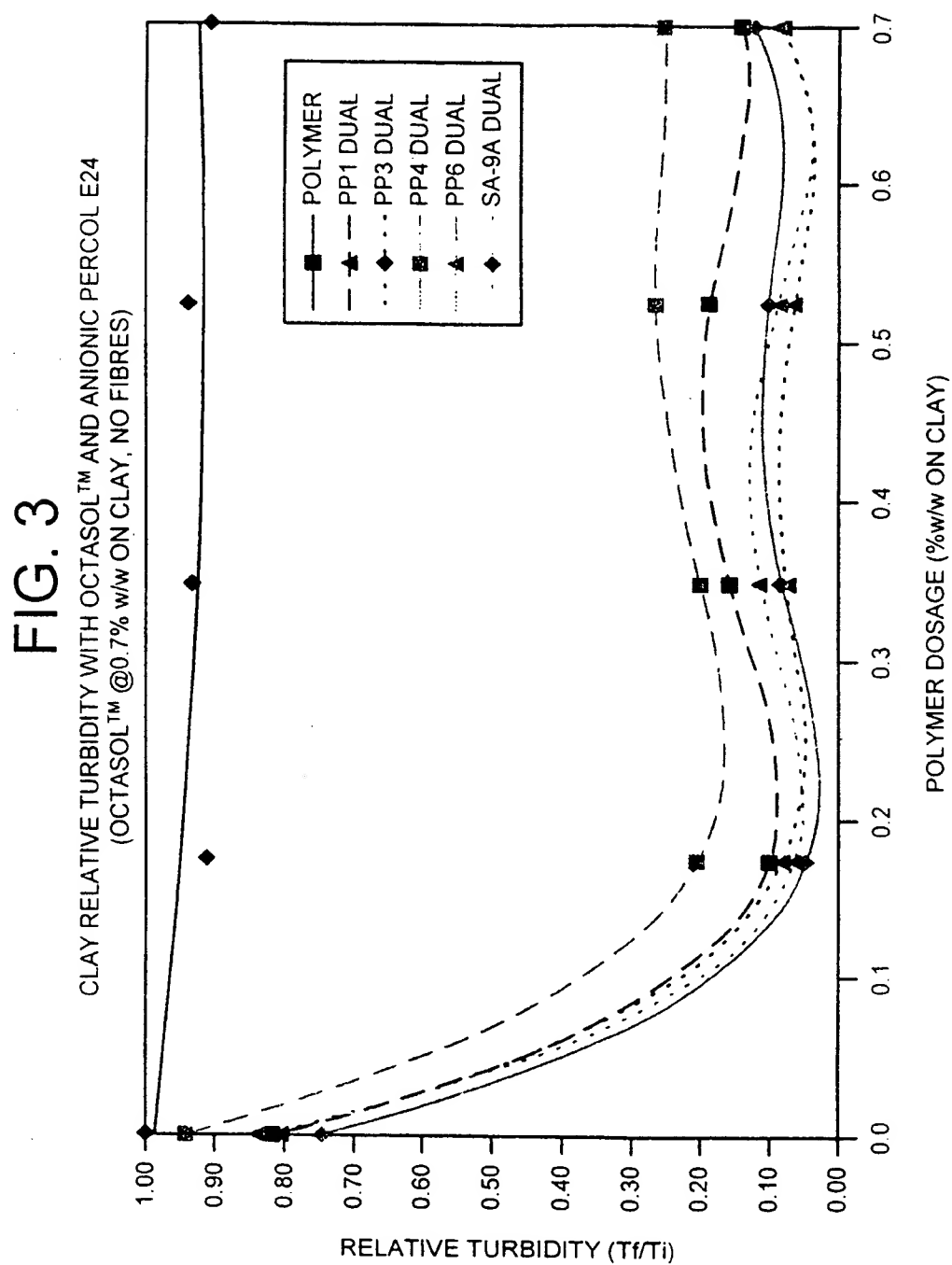(OCTASOL™ @0.7% w/w ON CLAY, NO FIBRES)

FIG. 4

CLAY FLOCCULATION WITH OCTASOL™ AND ANIONIC PERCOL E24
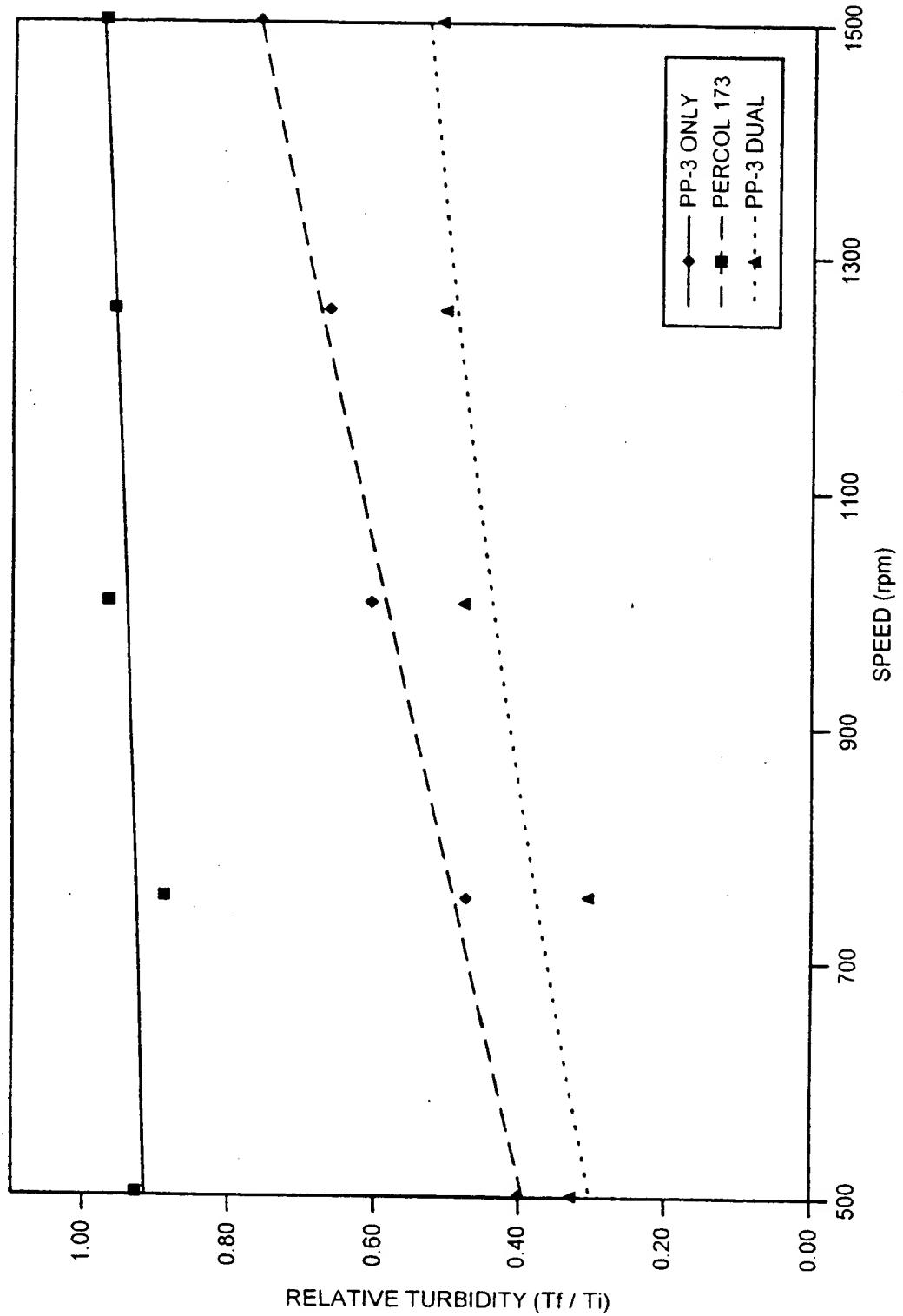(OCTASOL™ @ 0.7% w/w ON CLAY, NO FIBRES)

BNSDOCID: <WO   0053532A1 I >

FIG. 5

EFFECT OF pH ON CLAY FLOCCULATION WITH FIBRES

5% w/w CLAY SUSPENSION; 0.5% w/w PULP SLURRY; 20% CLAY ON FIBRE;
0.104% OCTASOL™; 0.026% PERCOL 173 POLYMER; 0.13% DUAL SYSTEM
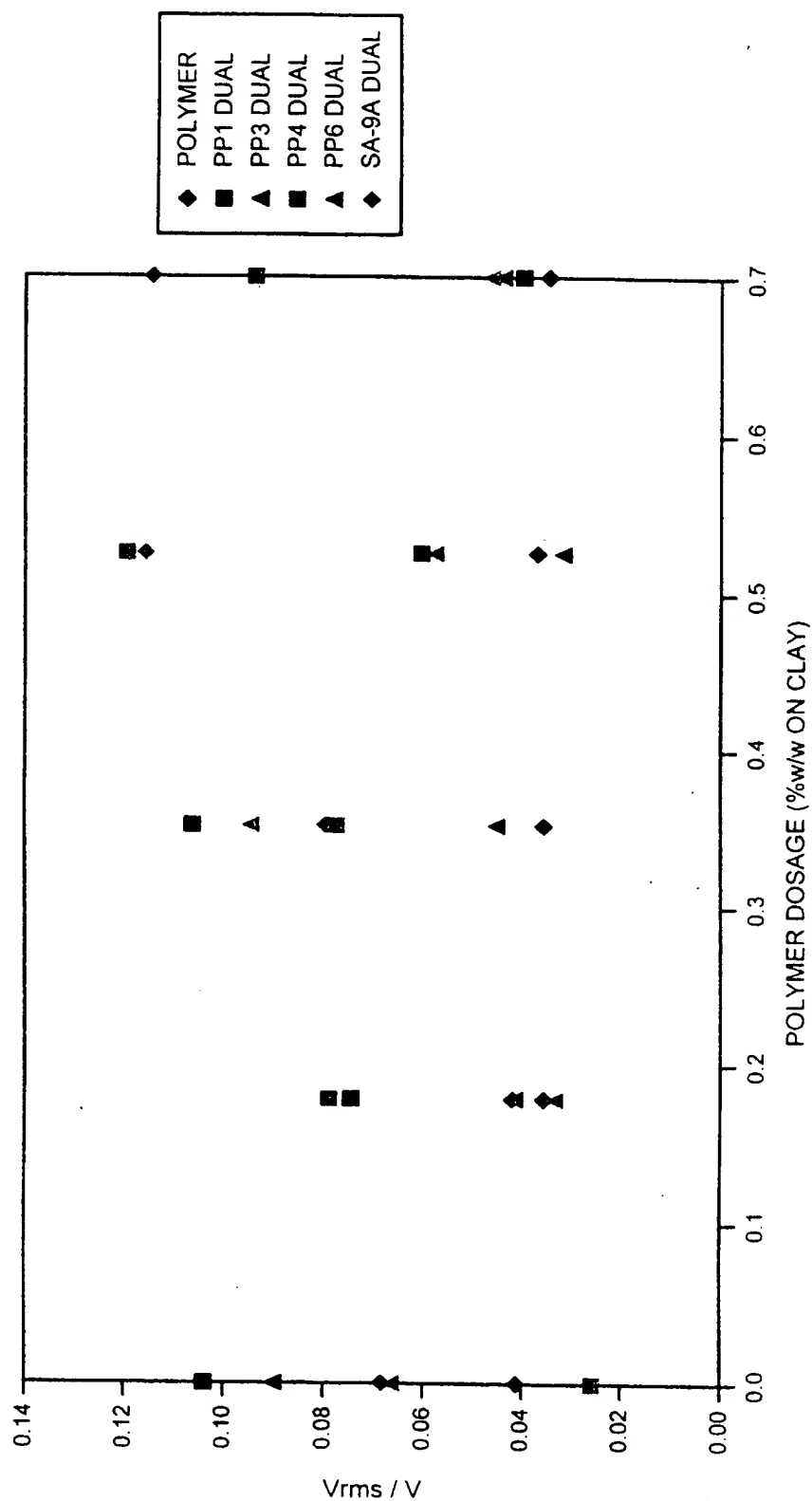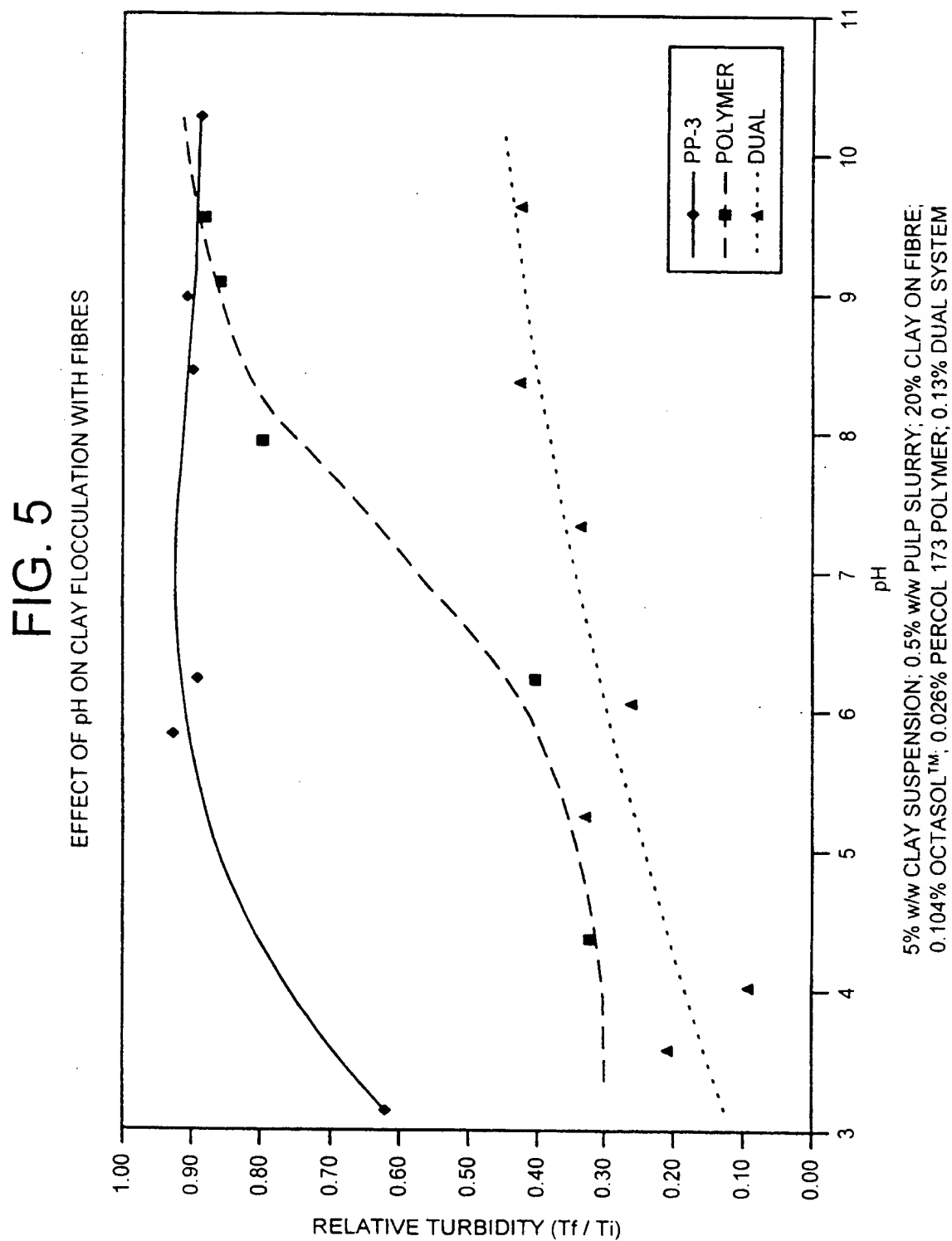
FIG. 6

VARYING PROPELLOR SPEED WITH FIBRE AND CLAY FILLER

5% w/w CLAY SUSPENSION; 0.5% w/w PULP SLURRY; 20% CLAY ON FIBRE;
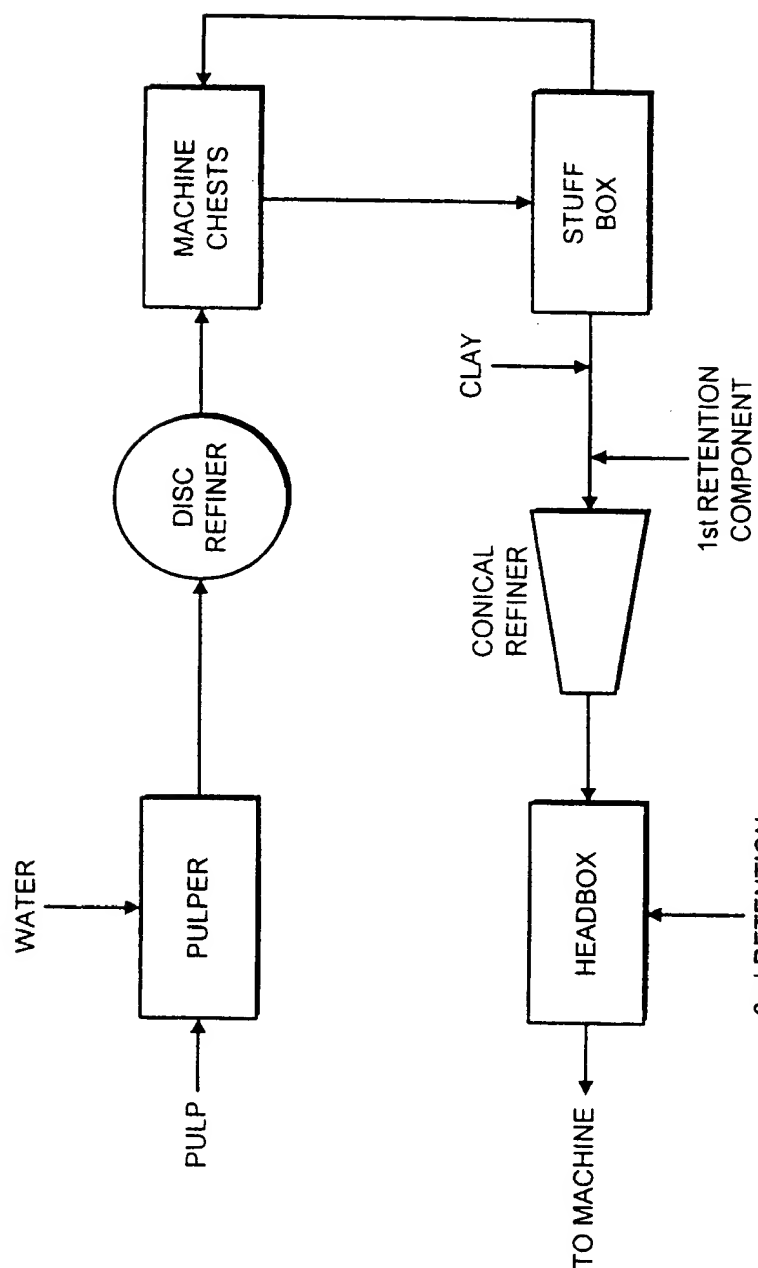0.104% OCTASOL™. 0.026% PERCOL 173 POLYMER; 0.13% DUAL SYSTEM

FIG. 7

SCHEMATIC OF MACHINE TRIAL WEST END PROCESS

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C02F1/52   D21H21/10   //D21H13:48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C02F   D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 41063 A (MATTHEWS DEREK PETER ;SIPPEL ROY JOSEPH (US)) 6 November 1997 (1997-11-06) cited in the application page 4, line 31 -page 5, line 1 page 37, line 20 -page 44, line 26; claims 12-21 ---	17,21
A	US 4 798 653 A (RUSHMERE JOHN D) 17 January 1989 (1989-01-17) cited in the application ---	
A	US 4 946 557 A (SVENDING PER J) 7 August 1990 (1990-08-07) cited in the application --- -/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2000	18/01/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Songy, O

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication.where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 915 475 A (BUGOSH J) 1 December 1959 (1959-12-01) cited in the application -----	

INTERNATIONAL SEARCH REPORT

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